Radiological, Chemical, and Biological Decontamination Using Atmospheric-Pressure Plasmas

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Researchers at LANL have applied a technology known as the atmospheric-pressure plasma jet (APPJ) to the decontamination of radiological, chemical, and biological agents from surfaces. [This unique technology (Figure 1) was invented at LANL in 1995[1] and won an R&D 100 Award in 1999.] An APPJ[2,3] produces a gas stream of highly reactive chemical species identical to those currently used by the semiconductor industry to clean silicon wafers. The APPJ reactor, however, creates non-thermal plasmas that can clean surfaces in "open air" instead of in vacuum. [The electrons, ions, and neutral-gas species that make up non-thermal plasmas are not in thermal equilibrium. The electrons are energetic ("hot"), whereas ions and neutral gases are near ambient temperature ("cool")]. The open-air concept eliminates the cost, time, and effort previously required to plasma-process work pieces in special vacuum chambers and, as a result, opens up a host of new plasma-processing applications. Although the effluent of the APPJ (Figure 1b) may appear somewhat like the flame of a Bunsen burner, its temperature can be maintained cooler than that of a hair dryer's exhaust. Chemically reactive species of oxygen generated by an APPJ device essentially "burn" many organic materials, such as oil and grease, from surfaces at these relatively low temperatures.

APPJ technology is used in a number of industrial and military applications. In materials processing, for example, applications range from etching silicon wafers to modifying surfaces to increase their wettability or absorption. Applications involving chemical and decontamination processing include the destruction of chemical and biological warfare (CBW) agents and the removal of radionuclides from surfaces and equipment. The development of this unique technology spans the regimes of bench-top studies to prototype demonstrations.

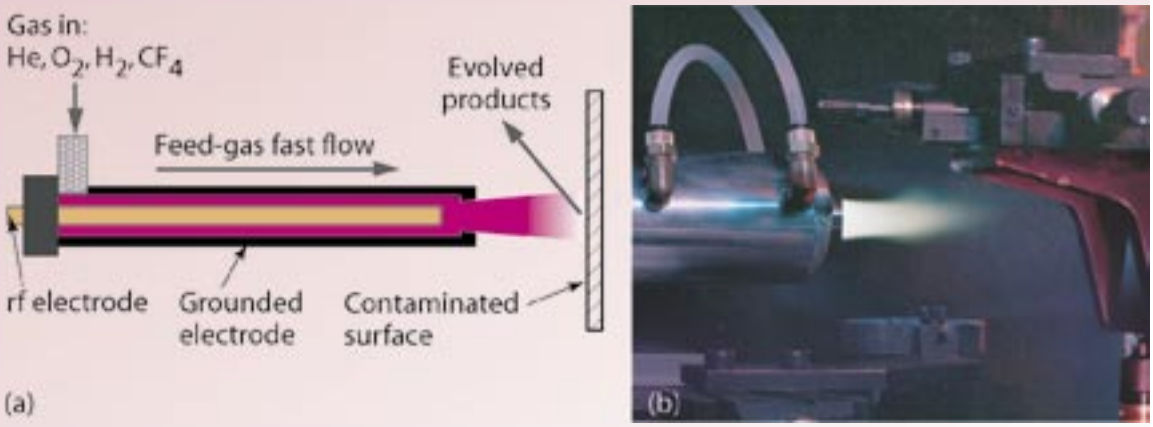

Figure 1. (a) Schematic of an rf-driven APPJ. (b) Photo of the APPJ device in operation.

Atmospheric-Pressure Plasma Jet

The APPJ produces a non-thermal, glow-discharge plasma operating at atmospheric pressure. The discharge uses a feed gas consisting primarily of an inert carrier gas, such as helium, and a small amount of an additive (e.g., O_2) that is activated. The feed gas flows between an outer, grounded, cylindrical electrode and an inner, coaxial electrode powered at an rf of 13.56 MHz (Figure 1a). The electric field produced between the electrodes causes the gas to breakdown into a "plasma state," or an ionized gas capable of conducting electricity. While passing through the plasma, the feed gas becomes excited, dissociated, or ionized by interacting with energetic electrons. Once the gas exits the discharge volume, ions and electrons are rapidly lost via a process known as recombination. Metastable species and radicals are left behind. Oxygen-containing plasmas, for example, produce reactive oxygen species, such as metastable oxygen (O_2^*), atomic oxygen (O), and oxygen ions (O_2^+). These reactive species tend to live relatively longer than electrons and ions and readily oxidize, or combust, many organic compounds on surfaces, including oil and grease.

Plasma feed gases can easily be tuned to produce tailor-made chemistry. For instance, hydrogen can be added in place of O_2 to produce a reducing environment of atomic hydrogen. CO_2 can be used in place of O_2 to minimize the amount of generally unwanted ozone (O_3), which tends to form downstream of an oxygen discharge. Reactive species can be directed onto a contaminated surface at high velocity where they can selectively neutralize organic materials without damaging the underlying surface. The temperature of this gas discharge typically ranges from 50°C to 300°C, which allows for plasma processing of sensitive materials and equipment at low temperatures and accelerated processing of more robust surfaces at higher temperatures.

"Polishing" Actinide-Contaminated DynEx Vessel Surfaces

Members of P-24, in collaboration with the Actinide Analytical Chemistry Group of the Chemistry Division at LANL, are conducting an Environmental Management Science Program (EMSP) to demonstrate general-purpose decontamination of superficial actinide contamination. The EMSP provides the science base for the APPJ application.

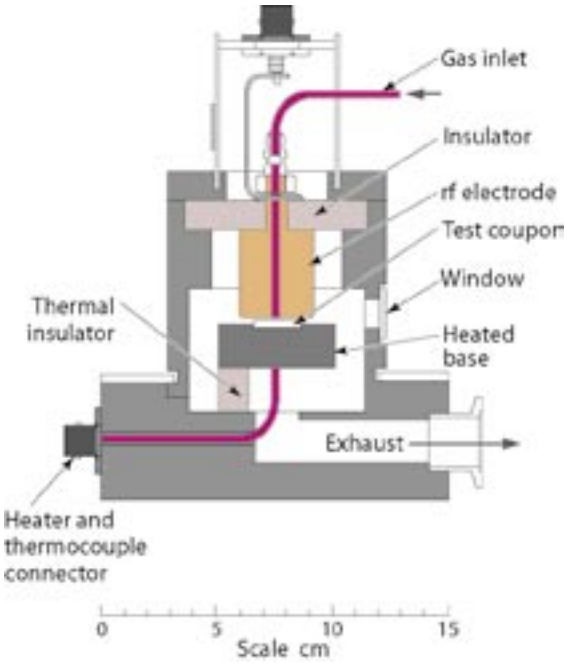

Figure 2. Schematic of the APPJ device used for actinide- and surrogate-actinide-etching studies.

In addition to this general decontamination project, we are investigating APPJ technology as a means to fully satisfy the special needs of the DynEx program in a cost-effective manner. DynEx studies are a required capability for the nuclear weapons program in general and for stockpile stewardship and weapons and weapons-component certification. These studies also provide data essential for the analysis and understanding of weapons-performance issues.

The current technology used for surface decontamination of residual waste from plutonium-processing operations (gloveboxes, tools, pipes, etc.) involves an acid-wash process that generates many liters of mixed-hazardous waste per unit. Moreover, this process requires nearly 8 hours of manual labor and results in considerable personnel radiation exposure. APPJ-plasma processing provides a convenient and waste-free method for decontaminating surfaces and recovering residual quantities of actinides (e.g., plutonium, uranium) that form volatile fluorides. In this method, a plasma generates a reactive chemical "intermediate" (e.g., fluorine atoms) from an inert feed gas (CF_4 or NF_3). This intermediate reacts with an actinide-contaminated surface to form a volatile gaseous product that is then pumped off the surface, leaving

it clean and decontaminated. The off-gas from this procedure is sent through a filtration system that traps and recovers any residual product. Known as "Atmospheric Pressure Decontamination (APD) DynEx Vessel Polishing," the goal of this DOE Defense Programs project is to determine whether the APPJ technology can decontaminate plutonium and uranium from metal surfaces, like actinide-contaminated DynEx vessels, in a *dry, safe* manner.

In APD-etching studies, 1/8-in.-thick, 1-in.-diam stainless steel coupons (disks) were impregnated with small amounts of plutonium and uranium and then exposed to an APPJ effluent. The APPJ device (similar to the one shown in Figure 2) contains a coupon holder and a stage for heating the coupons. The APPJ and associated enclosure are placed inside a glovebox at the Chemistry and Metallurgical Research Facility at LANL. The APPJ was operated at 700 W. About 90% of the uranium was removed in 10 minutes, whereas about 50% of the plutonium was removed in the same amount of time. The plutonium-doped coupons were further exposed at 10-minute intervals (Figure 3). We have also used *surrogate* actinide materials, such as tantalum and tungsten, in etching studies to safely test and evaluate the APPJ technique without the handling hazards and safeguards associated with actinide materials. In these studies, small quantities of NF_3, CF_4/O_2, or SF_6 were added to the primary helium feed gas to produce chemically active atomic fluorine. Using the APPJ method, removal of the actinide surrogate, tantalum, was demonstrated at > 10 μm per minute.

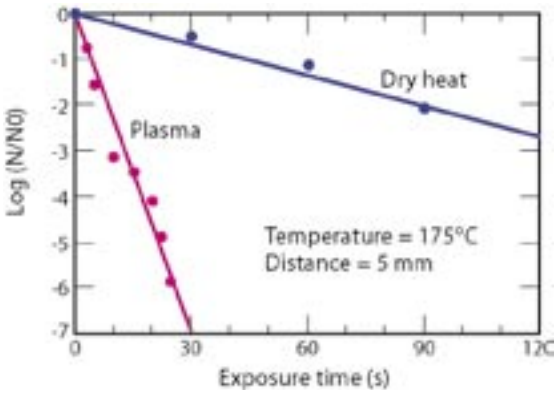

Figure 4. Destruction of the Anthrax surrogate BG using the APPJ method as compared to the dry-heat treatment.

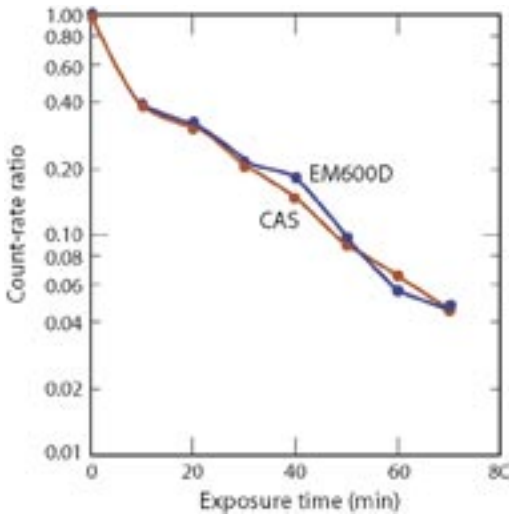

Figure 3. Removal data for plasma processing of plutonium-doped disks (ratio of counts at a given exposure time to counts with no exposure, i.e., initial activity).[4] CAS is an acronym for Canberra Alpha Spectrometer, and EM600D is the Eberline radiation monitor.

Chemical and Biological Weapons Decontamination

Events that happened in the U.S. after September 11, 2001, confirmed that chemical and/or biological agents could be used to inflict terror on civilians and to damage the infrastructure of our nation. Technology is therefore needed not only to detect these horrific weapons but also to reclaim and restore normal activities by decontaminating the areas targeted by CBWs. The P-24 CBW program at LANL is focused on the development of an all-dry, decontamination APPJ process suitable for use on sensitive equipment, such as computers, industrial machinery, and communications centers. As such, the "downstream" APPJ system developed for this program is portable, inexpensive, spot-specific for treatment, and amenable for use with objects of any size. It was used in tests to destroy biological- and chemical-warfare-agent surrogates, as well as actual chemical-warfare agents.[5] Active species produced inside the APPJ are rapidly blown out of the source and impinge a target surface 2 to 10 mm downstream. Most often, a He/O_2 feed gas is used, which produces a mix of atomic oxygen, metastable molecular oxygen, and small amounts of ozone. Figure 4 shows the results for decontamination of Bacillius globigii (BG), a surrogate for Anthrax spores, for both plasma and dry-heat treatments.

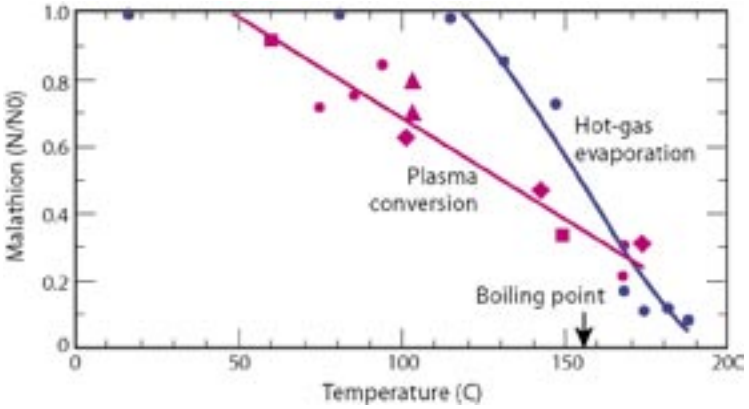

Figure 5. Destruction of the chemical-warfare surrogate, Malathion, using the APPJ method as compared to the dry-heat treatment. (Note: the plasma case has multiple symbols, representing more than one experiment.)

(The dry-heat treatment blows hot air, or some other gas, onto the biological agent.) Results indicate a seven-log kill (i.e., a factor of 10 million removal or decrease of the contaminate) of BG spores in 30 s with an APPJ effluent temperature of 175°C—which is ten times faster than dry heat at the same temperature! The APPJ also decontaminated surrogates for sulfur mustard and VX nerve agent and for actual VX. Figure 5 shows the results for the decontamination of Malathion (a pesticide surrogate for the chemical-warfare agent VX) for the plasma and dry-heat treatments.

Conclusion

In the near future, we will carry out parametric studies to determine the effect of gas mixture, coupon temperature, power, and gas-flow rates in an attempt to optimize the removal of plutonium and uranium from metal surfaces. If those studies indicate sufficient efficacy for the process, we will conduct scale-up studies to aid in the design of systems for decontaminating actual vessels or larger quantities of contaminated metals.

References

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Acknowledgment

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